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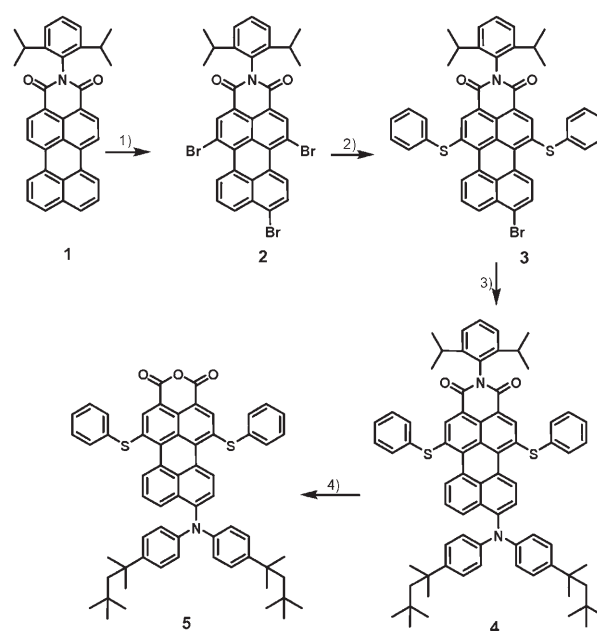
# An Improved Perylene Sensitizer for Solar Cell Applications

Chen Li,<sup>[a]</sup> Jun-Ho Yum,<sup>[b]</sup> Soo-Jin Moon,<sup>[b]</sup> Andreas Herrmann,<sup>[c]</sup> Felix Eickemeyer,<sup>[d]</sup> Neil G. Pschirer,<sup>[d]</sup> Peter Erk,<sup>[d]</sup> Jan Schöneboom,<sup>[d]</sup> Klaus Müllen,<sup>[a]</sup> Michael Grätzel,<sup>[b]</sup> and Mohammad K. Nazeeruddin<sup>\*[b]</sup>

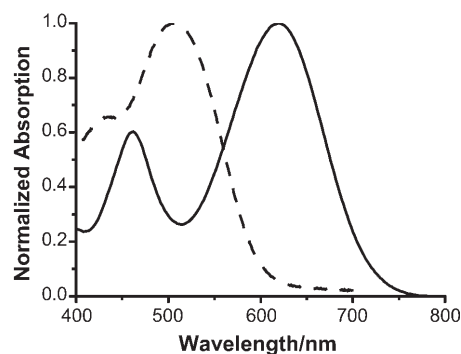
Dye-sensitized solar cells (DSSCs) based on nanocrystalline semiconductors have been the subject of intense investigation owing to their potential low cost, easy processing and good performance.<sup>[1]</sup> In these cells, a dye monolayer is adsorbed on a mesoporous film of titania. Upon light absorption, the dye injects electrons into the TiO<sub>2</sub> conduction band, where they are transported to the anode. The neutral dye is regenerated by electron transfer either from an electrolyte containing a redox system or from a solid-state hole conductor. With a closed external circuit and under illumination, the device then constitutes a photovoltaic energy-conversion system, which is regenerative and stable. In this technology, ruthenium complexes maintained a clear lead in performance amongst the thousands of dyes tested, yielding power conversion efficiencies of 10–11%.<sup>[2]</sup> However, in view of the cost and availability of 4d metals as well as their environmental non-compatibility, many metal-free organic dyes have been developed.<sup>[3]</sup>

As metal-free dyes, perylene derivatives have been widely applied in various optical devices owing to their outstanding chemical, thermal and photochemical stability and non-toxicity.<sup>[4]</sup> Several perylene dyes have been used as sensitizers in DSSCs, however, they exhibited very low overall power conversion efficiencies ( $\eta = 1\text{--}2\%$ ).<sup>[5]</sup> Recently, we reported diphenylamino-substituted perylene monoanhydrides as sensitizers which show an improved efficiency of up to 3.9%.<sup>[6]</sup> Herein, we present a novel perylene molecule **5** that bears two thiophenol groups in the 1 and 6 positions (see Scheme 1 and Experimental Section). Substituents at the 1 and 6 positions in perylene tune the HOMO and LUMO energies and thereby the absorption wavelength of the molecule. Another aspect of introducing (bulky) side groups is their ability to suppress dye aggregation on TiO<sub>2</sub> resulting in more efficient electron injection.<sup>[7]</sup> In this type of molecule, light absorption is associated with an intramolecular charge transfer (ICT) excitation from the donor to the acceptor moiety of the dye, which is anchored to the surface of the TiO<sub>2</sub>, resulting in efficient electron transfer from the excited dye into the TiO<sub>2</sub> conduction band.

Figure 1 shows the UV/Vis absorption spectra of **5** measured in CH<sub>2</sub>Cl<sub>2</sub> solution and adsorbed on a TiO<sub>2</sub> electrode. The solution absorption spectrum of **5** shows two peaks at  $\lambda = 620\text{ nm}$  ( $\epsilon = 22\,727\text{ M}^{-1}\text{ cm}^{-1}$ ) and at  $462\text{ nm}$  ( $\epsilon = 13\,704\text{ M}^{-1}\text{ cm}^{-1}$ ). From time-dependent density functional theory (DFT) calculations<sup>[8]</sup> at the B3LYP/TZVP level,<sup>[9,10]</sup> the first excitation (predicted at  $\lambda = 639\text{ nm}$ ) corresponds to the ICT from the HOMO located mainly on the diphenylamino group to the LUMO ( $\pi^*$ ) located



**Scheme 1.** Synthesis of **5**. 1) Br<sub>2</sub>, chloroform, reflux, 6 h, 86%; 2) thiophenol, K<sub>2</sub>CO<sub>3</sub>, NMP, RT, 3 h, 56%; 3) di(*p*-*tert*-octylphenyl)amine, [Pd<sub>2</sub>(dba)<sub>3</sub>], P(*t*Bu)<sub>3</sub>, *t*BuONa, overnight, 83%; 4) KOH, isopropanol, overnight, 80%. (dba = dibenzylideneacetone.)



**Figure 1.** Normalized UV/Vis absorption spectra of **5** in dichloromethane (solid line) and adsorbed on a nonocrystalline 6- $\mu\text{m}$  transparent TiO<sub>2</sub> film (dashed line).

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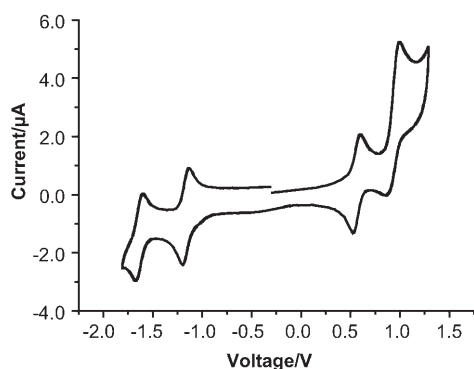
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mainly on the perylene. The second band (predicted at  $\lambda = 473$  nm) is a transition from a mixed thiophenyl-perylene  $\pi$  orbital to the LUMO. When absorbed onto  $\text{TiO}_2$ , compound **5** shows a blue-shifted absorption ( $\lambda_{\text{max}} = 506$  nm). This effect is attributed to the ring opening of the anhydride group on the perylene to form two carboxylates, which provide strong chemical interactions with the oxide surface. This phenomenon is well known for perylene anhydride sensitizers.<sup>[5,6]</sup>

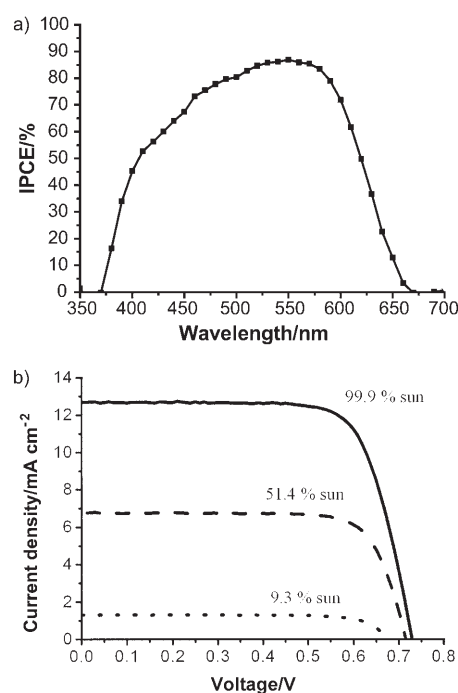
Figure 2 shows the cyclic voltammogram<sup>[11]</sup> of **5** which exhibits reversible waves both in the oxidation and reduction regions, indicating the electrochemical stability of **5**, a vital pa-



**Figure 2.** Cyclic voltammetry (CV) traces of **5** measured in a  $\text{CH}_2\text{Cl}_2$  solution containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) as supporting electrolyte. The reference electrode was an Ag wire internally calibrated with ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) in the measurement.

rameter for the durability of solar cells. The HOMO and LUMO are observed at 0.48 V and  $-1.08$  V (vs  $\text{Fc}/\text{Fc}^+$ ), respectively. When the dye adsorbs to  $\text{TiO}_2$ , it undergoes a transition to the dicarboxylate, that is, a ring-opened structure, which results in a negative shift in the HOMO potential. From DFT calculations of the anhydride and the dicarboxylate, we obtain a shift of 0.5 eV in the ionization potential. Also, the optical gap is increased upon ring opening to the dicarboxylate, resulting in an additional negative shift to the injecting excited-state energy level (see above). Hence, the energetic alignment of the HOMO and LUMO of the dye is well suited for electron injection into the  $\text{TiO}_2$  conduction band as well as regeneration by the triiodide/iodide redox couple or alternatively by a hole conductor.

To fabricate the solar cell, a 6- $\mu\text{m}$  thick transparent mesoporous  $\text{TiO}_2$  with 4- $\mu\text{m}$  thick scattering mesoporous  $\text{TiO}_2$  was prepared and treated with a 40 mM solution of titanium tetrachloride using a previously reported procedure.<sup>[1b]</sup> The films were heated at  $500^\circ\text{C}$  in air and sintered for 30 min before use. The solutions of sensitizer **5** were prepared in chlorobenzene at a concentration of 0.15 mM. The films were immersed into the dye solution for 16–18 h at room temperature and were then rinsed with acetonitrile to remove any unadsorbed dye and used as such for photovoltaic measurements in completely sealed devices. Figure 3 shows the incident monochromatic photon-to-current conversion efficiency (IPCE) and the  $J$ – $V$  (current density vs voltage) curve for the solar cell sensitized



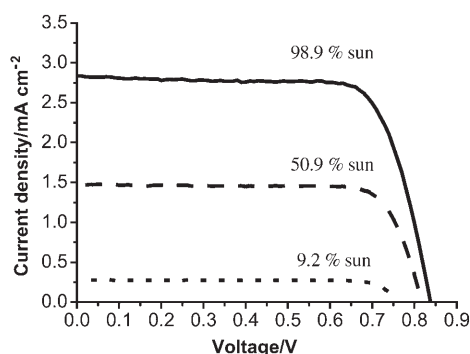
**Figure 3.** a) IPCE spectrum and b)  $J$ – $V$  curve of **5**-sensitized solar cells based on a volatile electrolyte (active area  $0.2\text{ cm}^2$ ). The redox electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M iodine, 0.1 M LiI and 0.5 M *tert*-butylpyridine in 15:85 (v/v) valeronitrile/acetonitrile.

with **5**. The IPCE curve of **5** plotted as a function of excitation wavelength exhibits a strikingly high plateau value of 87%.

The solar cell sensitized with **5** shows an unprecedented efficiency under solar simulated light irradiation ( $100\text{ mW cm}^{-2}$ , 1.5 AM global) of 6.8% with a short-circuit current density  $J_{\text{sc}} = (12.60 \pm 0.20)\text{ mA cm}^{-2}$ , an open-circuit voltage  $V_{\text{oc}} = (728 \pm 15)\text{ mV}$  and a fill factor  $\text{FF} = 0.74 \pm 0.01$ . As far as we know, this is the highest efficiency ever reported for a perylene/ $\text{TiO}_2$  DSSC. Integrating the IPCE curve over the solar spectrum results in a short-circuit current of  $11.8\text{ mA cm}^{-2}$  in agreement with the photocurrent of the measured device. At the low intensities, 9.3 and 51.4% sun, the  $J_{\text{sc}}$  values are 1.24 and  $6.74\text{ mA cm}^{-2}$ , respectively, which are linearly proportional to the light intensity. The efficiencies at 9.3 and 51.4% sun are 6.7 and 7.0%, respectively.

We fabricated complete solid-state dye-sensitized solar cells, where 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD) as an organic hole-transporting material replaces the liquid electrolyte. In this setup, interfacial hole transfer from the perylene sensitizer **5** to Spiro-MeOTAD takes place and regenerates the oxidized dye.<sup>[12]</sup> Figure 4 shows the solid-state solar cell  $J$ – $V$  characteristics measured under AM 1.5 solar conditions. At  $100\text{ mW cm}^{-2}$ ,  $J_{\text{sc}} = 2.83\text{ mA cm}^{-2}$ ,  $V_{\text{oc}} = 838\text{ mV}$  and  $\text{FF} = 0.75$  and the corresponding power conversion efficiency is 1.78%. The cell demonstrated an almost linear behavior under different light intensities ranging from 9.2 to 99% sun with a slightly higher efficiency ( $\sim 1.84\%$ ) at low intensity.

In summary, we have molecularly engineered a highly efficient novel perylene sensitizer, which yields 87% IPCE and



**Figure 4.** Current–voltage characteristics obtained with solid-state solar cells derivatized with **5**.

6.8% power conversion efficiency under standard AM 1.5 solar conditions. We have also demonstrated the possibility to utilize perylenes for solid-state solar cells yielding 1.8% power conversion efficiency under standard illumination conditions. Comparing these results with other perylene sensitizers,<sup>[6]</sup> we conclude that the thiophenol groups in **5** contribute strongly to the obtained high efficiencies. Work to extend the spectral response of these sensitizers further into the red and near-IR spectral region is in progress.

## Experimental Section

*N*-(2,6-Diisopropylphenyl)-perylene-3,4-dicarboximide (**1**) was supplied by BASF-SE (Ludwigshafen). Di(*p*-tert-octylphenyl)amine was purchased from MP Biomedicals Inc. All other starting materials and catalysts were purchased from Aldrich, Acros or ABCR and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AMX250 NMR spectrometers using the residual proton or the carbon signal of the deuterated solvent as an internal standard. Chemical shifts are reported in parts per million. FD mass spectra were performed with a VG Instrument ZAB 2-SE-FDP. UV/Vis absorption spectra were recorded on a Perkin–Elmer Lambda 40 spectrophotometer. Elemental analyses were carried out by the Microanalytical Laboratory at the Johannes Gutenberg University.

The synthesis of *N*-(2,6-diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide (**2**, Scheme 1) was described before.<sup>[13]</sup>

**Synthesis of 3:** Compound **2** (1 g, 1.4 mmol), thiophenol (153 mg, 1.4 mmol) and potassium carbonate (128 mg, 1.4 mmol) were stirred in *N*-methylpyrrolidone (NMP, 80 mL) at room temperature. After 1.5 h, additional thiophenol (76 mg, 0.6 mmol) and potassium carbonate (128 mg, 1.4 mmol) were added to the reaction mixture, which was stirred at the same temperature for another 1.5 h. After cooling to room temperature, the reaction mixture was precipitated and washed with water and dried. The product was purified by column chromatography on silica gel using dichloromethane and pentane (1:4) as eluent to give a dark red solid (600 mg, 56%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ = 8.63 (d, *J* = 8 Hz, 1H), 8.50–8.41 (m, 4H), 8.11 (d, *J* = 8 Hz, 1H), 7.91 (t, 1H), 7.47–7.26 (m, 13H), 2.64 (m, 2H; CH isopropyl), 1.07 ppm (d, *J* = 7 Hz, 12H; CH<sub>3</sub> isopropyl); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ = 163.88 (C=O), 146.51, 136.02, 135.77, 135.49, 135.40, 135.10, 133.35, 133.31, 131.75, 131.70, 131.29, 131.10, 130.30, 129.83, 129.33, 128.61, 128.09, 127.32, 125.95, 125.83, 124.45, 120.96, 29.55 (CH isopropyl), 24.17 ppm (CH<sub>3</sub> isopropyl); MS: *m/z* 775.5 (100%) [*M*<sup>+</sup>] (calcd

776.82); IR (KBr):  $\tilde{\nu}_{\text{max}}$  = 2944, 1908, 1701, 1589, 1488, 1390, 1338, 1238, 1119, 1012, 938, 868, 810, 774, 725, 708, 655, 544 cm<sup>−1</sup>; elemental analysis (%) calcd for C<sub>46</sub>H<sub>34</sub>BrNO<sub>2</sub>S<sub>2</sub>: C 71.12, H 4.41, N 1.80, S 8.26; found: C 70.79, H 4.56, N 1.73, S 7.93; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 515 (4.47), 475 nm (4.46).

**Synthesis of 4:** A mixture of **3** (0.3 g, 0.39 mmol), di(*p*-tert-octylphenyl)amine (0.22 g, 0.58 mmol), [Pd<sub>2</sub>(dba)<sub>3</sub>] (20 mg, 0.022 mmol), tri-*t*-butylphosphine (20 mg, 0.10 mmol), sodium *tert*-butyl alcohol (55 mg, 0.57 mmol) and toluene (100 mL) was stirred at 80 °C under argon atmosphere overnight. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography using toluene as eluent on silica to give a green solid (0.35 g, 83%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ = 8.68 (d, *J* = 8 Hz, 1H), 8.52 (d, *J* = 7 Hz, 1H), 8.47 (s, 1H), 8.43 (s, 1H), 8.16 (d, *J* = 8 Hz, 1H), 7.52–7.27 (m, 19H), 7.01 (d, *J* = 9 Hz, 4H), 2.66 (m, 2H; CH isopropyl), 1.73 (s, 4H), 1.37 (s, 12H), 1.08 (s, 12H; CH<sub>3</sub> isopropyl), 1.08 (d, *J* = 7 Hz, 12H), 0.77 ppm (s, 18H); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ = 163.81 (C=O), 147.79, 146.55, 146.36, 145.17, 136.65, 136.55, 135.92, 135.80, 134.50, 133.17, 132.77, 132.19, 131.70, 131.65, 130.00, 129.92, 129.67, 129.23, 128.86, 128.56, 128.34, 127.57, 126.22, 125.08, 124.59, 124.24, 123.13, 120.37, 119.67, 57.38, 38.49, 32.66, 31.88, 31.62, 29.34 (CH isopropyl), 23.98 ppm (CH<sub>3</sub> isopropyl); MS: *m/z* 1088.9 (100%) [*M*<sup>+</sup>] (calcd 1089.57); IR (KBr):  $\tilde{\nu}_{\text{max}}$  = 2944, 2362, 1705, 1670, 1568, 1461, 1385, 1326, 1239, 1202, 1050, 937, 866, 829, 770, 725, 698, 562 cm<sup>−1</sup>; elemental analysis (%) calcd for C<sub>74</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 81.58, H 7.03, N 2.57, S 5.89; found: C 80.80, H 7.47, N 2.49, S 5.81; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 606 (4.14), 462 nm (3.89).

**Synthesis of 5:** A mixture of **4** (300 mg, 0.28 mmol), potassium hydroxide (500 mg, 9 mmol) and isopropanol (50 mL) was refluxed under stirring overnight. The reaction mixture was cooled down to room temperature and then poured into acetic acid, and the solution was stirred at 40 °C for 4 h. The solvent was removed in vacuum. The crude product was washed with water. Column chromatography using toluene as eluent on silica yielded **5** as a green solid (200 mg, 80%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ = 8.54 (d, *J* = 8 Hz, 1H), 8.45 (d, *J* = 7 Hz, 1H), 8.32 (d, *J* = 7 Hz, 2H), 8.20 (d, *J* = 8 Hz, 1H), 7.54–7.38 (m, 12H), 7.31 (d, *J* = 9 Hz, 4H), 7.02 (d, *J* = 9 Hz, 4H), 1.73 (s, 4H), 1.36 (s, 12H), 0.77 ppm (s, 18H); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, TMS): δ = 160.62 (C=O), 160.53, 148.47, 146.52, 145.44, 137.16, 137.03, 136.35, 135.72, 135.63, 135.49, 135.36, 134.40, 133.53, 133.12, 132.02, 131.87, 130.26, 130.19, 129.40, 129.22, 129.17, 129.06, 128.69, 128.02, 127.64, 127.29, 125.11, 124.09, 123.33, 116.07, 115.21, 57.37, 38.51, 32.65, 31.87, 31.61 ppm. MS: *m/z* 929.5 (100%) [*M*<sup>+</sup>] (calcd 930.29); IR (KBr):  $\tilde{\nu}_{\text{max}}$  = 3056, 2962, 2361, 1938, 1766, 1564, 1458, 1406, 1364, 1326, 1270, 11186, 1014, 980, 908, 830, 802, 770, 749, 688, 580, 548 cm<sup>−1</sup>; elemental analysis (%) calcd for C<sub>62</sub>H<sub>59</sub>NO<sub>3</sub>S<sub>2</sub>: C 80.05, H 6.39, N 1.51, S 6.89; found: C 79.96, H 6.38, N 1.43, S 6.87. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 620 (4.35), 462 nm (4.13).

Electrochemical experiments were carried out with an EG&G Princeton Applied Research potentiostat model 273. The working electrode consisted of an inlaid platinum disk (1.5-mm diameter) that was polished on a felt pad with alumina (0.05 μm) and sonicated in milli-Q water for 5 min before each experiment. A platinum wire was used as the counter electrode, and an Ag wire was used as the reference electrode internally calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) in the measurement.

**Dye-sensitized solar cells:** The photoanodes composed of nanocrystalline TiO<sub>2</sub> were prepared using a previously reported procedure.<sup>[1b]</sup> A paste composed of 20-nm anatase TiO<sub>2</sub> particles for the



transparent nanocrystalline layer was coated on FTO glass plates (Nippon Sheet Glass, 4 mm thickness) pretreated with  $\text{TiCl}_4$  (40 mM) by repetitive screen printing to obtain a thickness of 6  $\mu\text{m}$ . Then, a paste for the scattering layer containing 400-nm-sized anatase particles (CCIC, HPW-400) was deposited onto the transparent nanocrystalline layer. The resulting layer had a thickness of around 4  $\mu\text{m}$ . The  $\text{TiO}_2$  electrodes were gradually sintered under a programmed flow: at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and finally at 500 °C for 15 min. The  $\text{TiO}_2$  electrodes were treated again by  $\text{TiCl}_4$  under 70 °C for 30 min and sintered again at 500 °C for 30 min before they were dipped into dye solution. The  $\text{TiO}_2$  electrodes were immersed into the solutions of 5 (150  $\mu\text{M}$ ) in chlorobenzene and kept at room temperature for 16–18 h. The dye-adsorbed  $\text{TiO}_2$  electrode and thermally platinized counter electrode were assembled into a sealed sandwich-type cell with a gap of a hot-melt ionomer film (Surlyn, thickness 1702.25  $\mu\text{m}$ , DuPont). An electrolyte solution (0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M iodine, 0.1 M LiI and 0.5 M *tert*-butylpyridine in 15:85 (v/v) valeronitrile/acetonitrile) was used for the redox couple. To reduce scattered light from the edge of the glass electrodes of the dyed  $\text{TiO}_2$  layer, a light-shading mask was used onto the DSSCs so the active area of the DSSCs was fixed to 0.2  $\text{cm}^2$ .

For the solid-state solar cell, details of the process were described in a previous report.<sup>[12]</sup> The cell consists of a F-doped  $\text{SnO}_2$  glass substrate (15  $\Omega/\square$ , Pilkington) onto which a compact layer of approximately 100 nm was deposited by spray pyrolysis. The nanoporous layer (~1.8  $\mu\text{m}$ ) of 20-nm diameter  $\text{TiO}_2$  was coated by doctor-blading. After the  $\text{TiO}_2$  layer had been annealed at 500 °C for 30 min under oxygen flow, the film was treated with 0.02 M aqueous  $\text{TiCl}_4$  solution overnight. The  $\text{TiO}_2$  electrode was soaked in the dye solution and kept at room temperature for overnight. The hole-conducting matrix was applied by spin-coating of a solution of 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD) in chlorobenzene containing *tert*-butylpyridine and  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ . Fabrication of the device was completed by evaporating a 50-nm gold electrode on top. For the photovoltaic measurement of solid-state solar cells, their active areas were fixed to 0.14  $\text{cm}^2$ .

For photovoltaic measurements of the DSSCs, the irradiation source was a 450 W xenon light source (Osram XBO 450, USA), whose power of an AM 1.5 solar simulator was calibrated by using a Tempax 113 solar filter (Schott). The output power of an AM 1.5 solar simulator was calibrated by using a reference Si photodiode equipped with a colour-matched IR cutoff filter (KG-3, Schott) in order to reduce the mismatch in the region of 350–750 nm between the simulated light and AM 1.5 to less than 2%.<sup>[1b]</sup> The measurement delay time of *J*–*V* characteristics of DSSCs was fixed to 40 ms. The measurement of incident photon-to-current conversion efficiency (IPCE) was plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.).

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**Keywords:** dye-sensitized solar cells • fused-ring systems • photoelectrochemical cells • sensitizers

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